

# Nuclear Waste Glasses: Continuous Melting and Bulk Vitrification

Prepared for the U.S. Department of Energy  
Assistant Secretary for Environmental Management

**Office of River Protection**

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# **Nuclear Waste Glasses: Continuous Melting and Bulk Vitrification**

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**Abstract.** This contribution addresses various aspects of nuclear waste vitrification. Nuclear wastes have a variety of components and composition ranges. For each waste composition, the glass must be formulated to possess acceptable processing and product behavior defined in terms of physical and chemical properties that guarantee the glass can be easily made and resist environmental degradation. Glass formulation is facilitated by developing property-composition models, and the strategy of model development and application is reviewed. However, the large variability of waste compositions presents numerous additional challenges: insoluble solids and molten salts may segregate; foam may hinder heat transfer and slow down the process; molten salts may accumulate in container refractory walls; the glass on cooling may precipitate crystalline phases. These problems need targeted exploratory research. Examples of specific problems and their possible solutions are discussed.

## **Introduction**

The majority of nuclear waste in the world originates from the nuclear fuel cycle and nuclear weapons reprocessing [1]. At least 108 sites containing radioactive waste exist in the United States. Perhaps the most prominent among them is the Hanford Site in the State of Washington [2], where 177 underground radioactive waste tanks contain roughly 200,000 m<sup>3</sup> of radioactive liquid and sludge from plutonium production from 1944 to 1987.

Hanford Site waste will be pretreated and separated into high-level waste (HLW) and low-activity waste (LAW) fractions. Both HLW and LAW will be vitrified in continuous melters, and a substantial portion of the LAW will be partitioned to a supplemental LAW treatment. To make nuclear-waste glass, the waste streams from a pretreatment facility, in the form of HLW slurries or LAW solutions, are mixed with glass-forming and modifying additives in the HLW or LAW vitrification facilities, respectively. In both facilities, the resulting melter feeds are charged into electrically heated continuous melters from which the molten glass is poured into stainless-steel canisters for disposal in the Yucca Mountain repository or stainless-steel containers for disposal in the Hanford Integrated Disposal Facility.

This paper briefly reviews the glass-formulation method for making glasses that easily melt and meet the quality required for disposal. Also discussed are property-composition relationships, processing problems, and glass-durability issues.

## **Glass Formulation**

To make certain waste glass is easily processable and has a quality conforming to the regulatory requirements for disposal, the glass must be properly formulated for any waste composition (within

the defined range) that may be delivered from the waste pretreatment facility. These projected waste streams will substantially vary, both in the number and concentration ranges of major components.

Melt processability and product quality are defined in terms of glass properties. Glasses are formulated using mathematical relationships, also called models, that link key properties to glass composition. The models are expressed in terms of response functions, usually polynomials relating properties to mass or mole fractions of components; the numerical coefficients are determined by applying regression analysis to experimental data.

For continuous melters, glass properties that must be controlled to allow easy processing are the melt viscosity, electrical conductivity, and liquidus temperature. This is because the processing temperature in waste glass melters cannot exceed 1200°C; above this temperature, the Inconel® electrodes (a material that can withstand waste-melt corrosiveness) lose their mechanical strength.

The product quality of waste glasses is defined by means of outcomes of various standardized tests, such as the product consistency test [3], vapor hydration test [4], and toxicity characteristic leaching procedure [5]. The quality requirements are more restrictive for LAW glasses because these glasses will be less protected in the disposal facilities than HLW glasses in the repository. Economic criteria (glass volume and process rate) are also important and must be considered.

For most composition regions of waste glasses, first-order polynomials are sufficiently representative [6]; i.e.,  $P = f(\sum_{i=1}^N P_i x_i)$ , where  $P$  is the glass property,  $f$  is the response function (e.g., exp),  $x_i$  is the  $i$ -th component fraction (mass or mole) in glass, and  $P_i$  is  $i$ -th component property coefficient (partial specific or molar property).

As glass components originate from waste, additives, or both, they are subjected to mass balances in the form  $x_i = w_i W + a_i(1 - W)$ , where  $w_i$  is the  $i$ -th component fraction in the non-volatile portion of waste,  $a_i$  the  $i$ -th component fraction in non-volatile portion of additives, and  $W$  the waste loading (the fraction of glass that originated in the waste). Mathematically speaking, the task of glass formulation is to determine the optimum value of  $W$  and optimized values of  $a_i$ s that yield glass with acceptable properties for a given set of  $w_i$  values.

Because models are subjected to uncertainties, experimental confirmation is necessary before a glass is subjected to large-scale testing and production. Thus, glass formulation proceeds in the following steps:

- 1) For the given waste, determine a glass composition with optimized properties using property-composition relationships.
- 2) Prepare a simulant of the glass using nonradioactive surrogates and measure its key properties.
- 3) Compare measured and calculated properties and adjust the formulation if necessary.
- 4) Prepare the final simulant glass and measure its key properties.
- 5) Prepare glass from the actual waste and measure its key properties.

## Processing Problems

Not all processing problems can be avoided by formulating glasses with desirable properties. Unlike in the processing of commercial glasses, the feed composition of waste glasses is only partially controlled. This can lead to various problems described in this section.

As shown schematically in Fig. 1, the melter feed (waste plus additives that may be premelted into a frit) is charged into the continuous melter in the form of a water slurry that dries in the melter and forms a cold cap on the pool of molten glass (similar to batch pile or batch blanket of commercial-glass melters).

As presented in Fig. 2, various intermediate solids can form within the cold cap [7]. These solids can be transferred to the melter bottom by descending convection currents where they can settle (Fig. 3) and eventually block the melter outlet. If the bottom sludge is electrically conducting, it can distort the electric field in the melter.

Molten ionic salts (predominantly sulfates) tend to segregate during the melting process and accumulate on the melt surface, causing refractory corrosion. As presented in Fig. 4, undissolved sulfate is taken to the melt surface inside gas bubbles [8].

Also, foaming is often a serious problem. Melting reactions produce a large volume of gas of which a small fraction is trapped in the glass-forming melt and later released. More troublesome is the foam from bubbles released from molten glass from multivalent oxides such as  $\text{FeO}_x$ . This foam insulates the cold cap, slowing the transfer of heat needed for melting [9].

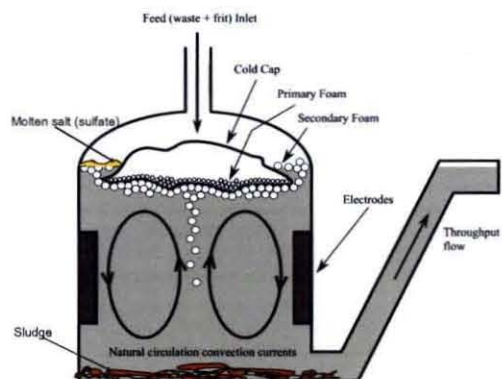


Fig. 1. Schematic of continuous waste-glass melter.

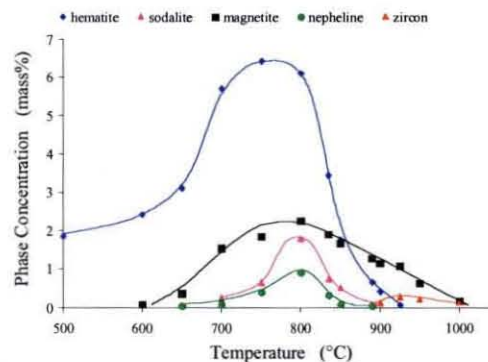


Fig. 2. Intermediate crystalline phases that form in a Savannah River waste glass [7].



Fig. 3. Micrograph of a melter-bottom sludge (spinel and silver) [10].



Fig. 4. Scanning electron Microscopy (SEM) image of sulfate bubble in an LAW glass [8].

Bulk vitrification has been recently designed as a supplemental process for vitrifying LAW. Dry feed is charged into a large (7.3×2.3×2.3 m) metallic box lined with layers of refractory and insulating materials and electrically heated with two graphite electrodes. The box is then sealed and used as a waste package for disposal.

Bulk vitrification is facing similar problems as those in continuous melting. Molten salts segregated on the melt surface may contain technetium (Tc) that is present in LAW in minute concentrations. Though precipitation and settling of the crystalline phase is not a problem, liquid metals can precipitate and accumulate at the container bottom. Metals can contain metallic Tc that can be easily released in a humid environment. Finally, releasable Tc can accumulate in the glass-contact refractory walls that are made from a relatively inexpensive castable refractory material. Molten salts (mainly nitrates) from LAW can migrate into these walls, driven by capillarity.

While methods for avoiding salt accumulation on the melt surface are currently being investigated, the other problems have been solved. Metal precipitation can be eliminated by using low-iron additives. The migration of salts into the walls was reduced to an acceptable level by increasing the specific surface area of the feed additives (using fine silica) and by cellulose additions that destroy a portion of nitrates at temperatures at which the salts are relatively immobile [11].

## Process Rate

The rate of melting is an important productivity issue, especially for continuous melters. The melting rate is controlled jointly by the heat-transfer rate and the rate of feed-to-glass conversion [9]. This can be expressed as

$$N = \frac{N_C^2}{2N_H} \left[ \left( 1 + \frac{4N_H^2}{N_C^2} \right)^{1/2} - 1 \right] \quad (1)$$

where  $N$  is the rate of melting (mass per time and area),  $N_C$  is the conversion-controlled rate of melting, and  $N_H$  is the heat-transfer-controlled rate of melting. These rates are defined as

$$N_C = \left[ \frac{k\rho\lambda_C(T_M - T_C)}{Q} \right]^{1/2} \quad (2)$$

and

$$N_H = \frac{\lambda_H(T_M - T_C)}{\delta Q} \quad (3)$$

where  $\lambda_C$  and  $\lambda_H$  are effective heat conductivities of the cold cap and molten glass,  $T_C$  and  $T_M$  are the temperatures of the cold cap and the bulk melt, respectively,  $\delta$  is the thermal-boundary-layer thickness,  $k$  is the conversion-rate coefficient,  $\rho$  is the feed density, and  $Q$  is the conversion heat (the energy needed to turn slurry feed under ambient conditions to 1 kg of glass). The thickness of the thermal boundary layer is defined as  $\delta = (T_M - T_i)/(\delta T/\delta y)_{y=0}$ , where  $y$  is the vertical distance from the cold-cap-melt interface and  $T_i$  is the temperature of the cold-cap-melt interface.

Both the heat transfer and the conversion process are upset if fluxes (that are present in the form of low-viscosity molten ionic salts, also called the primary melt, existing at temperatures at which the glass-forming melt has not yet developed) migrate out of the cold cap. This leads to cold-cap freezing and inability to reach a steady state in the melter.

An important factor affecting the heat-transfer rate is the melt viscosity, which influences the velocity of natural convection in the melter and the extent of bubble/foam accumulation under the cold cap [12]. Because viscosity depends on glass composition, glass formulation is of a crucial importance for melter operation. For fast melting, the viscosity near the cold-cap bottom surface should be as low as possible.

Heat can be transferred from the hot melt to the cold cap faster by increasing the melt temperature and by bubbling. A higher melt temperature increases the temperature gradient in the melt under the cold cap, thus increasing the density gradient, which is the driving force for melt circulation. Bubbling further enhances melt circulation, removes foam accumulated under the cold cap, and even breaks through the cold cap, exposing a larger interface area to melting. Increased melt circulation (by increased temperature, decreased viscosity, and bubbling) suppresses the thermal boundary layer under the cold cap, increasing the heat flux to the cold cap.

Note that Eq. 2 grossly oversimplifies the conversion process by reducing a rather complex set of parallel and sequential reactions and transitions with one rate coefficient,  $k$ . In reality, the conversion process proceeds in several stages. As the feed temperature increases, the ionic salts begin to melt, forming the primary melt. The reactive components of the primary melt, such as carbonates and nitrates, react with silica, creating the glass-forming melt while leaving behind less-reactive sodium sulfate that only gradually dissolves in the glass-forming melt. Once the glass-forming melt connects into a continuous body, the residues of molten salts and oxidation-reduction reactions generate gases that are trapped inside the melt in the form of bubbles. The resulting

primary foam increases the melt volume several times [12] and collapses as soon as the melt viscosity decreases below a certain level. These stages are common to waste and commercial feeds and batches.

The complexity of the feed-to-glass conversion process indicates that its rate can be influenced by many internal parameters. Probably most prominent among them is the content of reductants, such as sugar or cellulose, in the feed. Reductants react with oxyionic salts, especially nitrates and nitrites, and with high-valence oxides, such as  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$ . These reactions are exothermic: They internally supply heat to the cold cap independent of heat transfer from external sources. Also, reducing the content of ionic salts in the cold cap decreases the potential for flux separation that leads to cold-cap freezing. The importance of reductants for bulk vitrification has been mentioned above.

The impact of the primary foam on the rate of melting is not well understood. It is not clear whether the main effect of primary foam is insulating the cold cap or whether the growing bubbles help to homogenize the melt, thus helping dissolve the solid particles.

### **Product Quality Issues: Long-Term Corrosion**

As stated above, glass acceptability for disposal is defined by responses to standard corrosion tests. Glass corrosion is a function of thermodynamic state variables (temperature and composition) as well as the kinetics of various individual reactions that participate in the corrosion process. It is not well understood at present how the responses of glass to standard tests relate to long-term corrosion behavior, especially when considering the poor predictability of the environmental conditions over the hundred-thousand years that the radioactivity needs to decay.

Under laboratory conditions in a closed system, glass corrosion proceeds in four stages: initial stage, solution-saturation stage, transition stage (a catastrophic event), and final stage. The transition stage occurs when mineral species suddenly precipitate from the oversaturated solution. In the final stage, glass dissolution is controlled by the aqueous reactions. It is not clear whether these two final stages can occur in the open system.

The long-term behavior of glass is usually simulated by accelerated tests, such as a vapor hydration test, where glass coupons are exposed to hot steam. Fig. 5 shows examples of glasses fully or strongly corroded [4], i.e., turned into mineral gels and crystals; it also shows examples of crystalline phases usually seen on the coupon surfaces.

As the melt is poured into canisters, some of it is rapidly quenched when contacting the canister walls, while the melt cools at the slowest rate in the canister centerline (Fig. 6). Even a slower rate is experienced by glass in the center of the bulk-vitrification box. During slow cooling, the glass may precipitate crystals (Fig. 6) that remove components from the amorphous matrix, thus changing its corrosion resistance. Common crystalline phases found in Hanford HLW glasses are spinel  $[(\text{Fe},\text{Ni},\text{Zn})(\text{Fe},\text{Cr},\text{Mn})_2\text{O}_4]$ , hematite ( $\text{Fe}_2\text{O}_3$ ), zircon ( $\text{ZrSiO}_4$ ), baddeleyite ( $\text{ZrO}_2$ ), parakelydshite ( $\text{Na}_2\text{Zr}_2\text{SiO}_7$ ), nepheline ( $\text{NaAlSiO}_4$ ), wollastonite ( $\text{CaSiO}_3$ ), and cristobalite ( $\text{SiO}_2$ ). Most of these phases do not form in a sufficient quantity to influence glass durability. However, a massive precipitation of nepheline can significantly decrease glass durability and must be avoided.



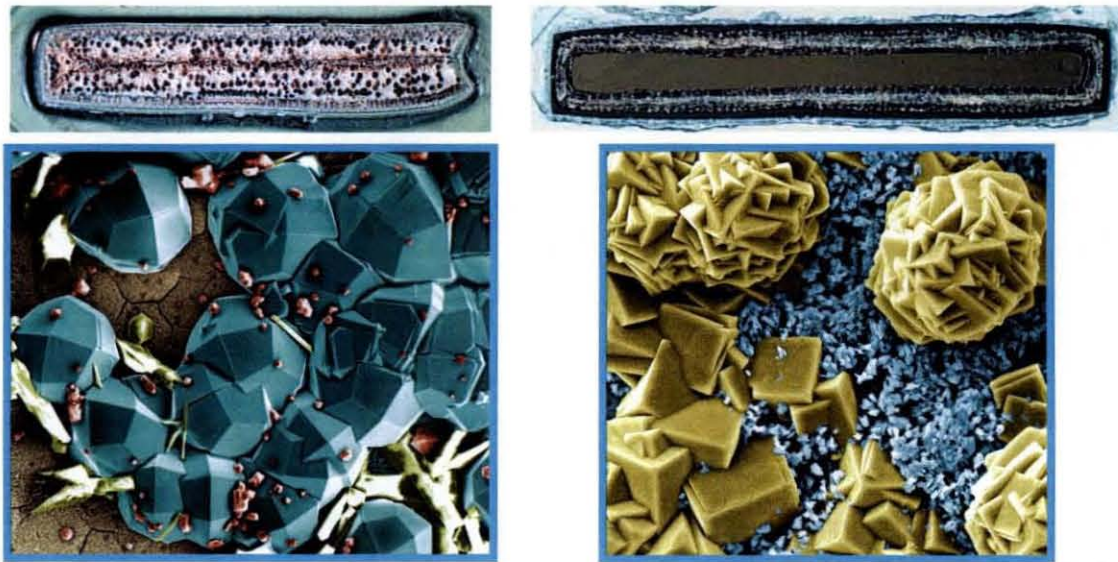


Fig. 5. Corroded vapor-hydration-test coupons; top: two examples of thin sections (optical images); bottom: zeolite crystals on coupon surfaces (colored SEM images).

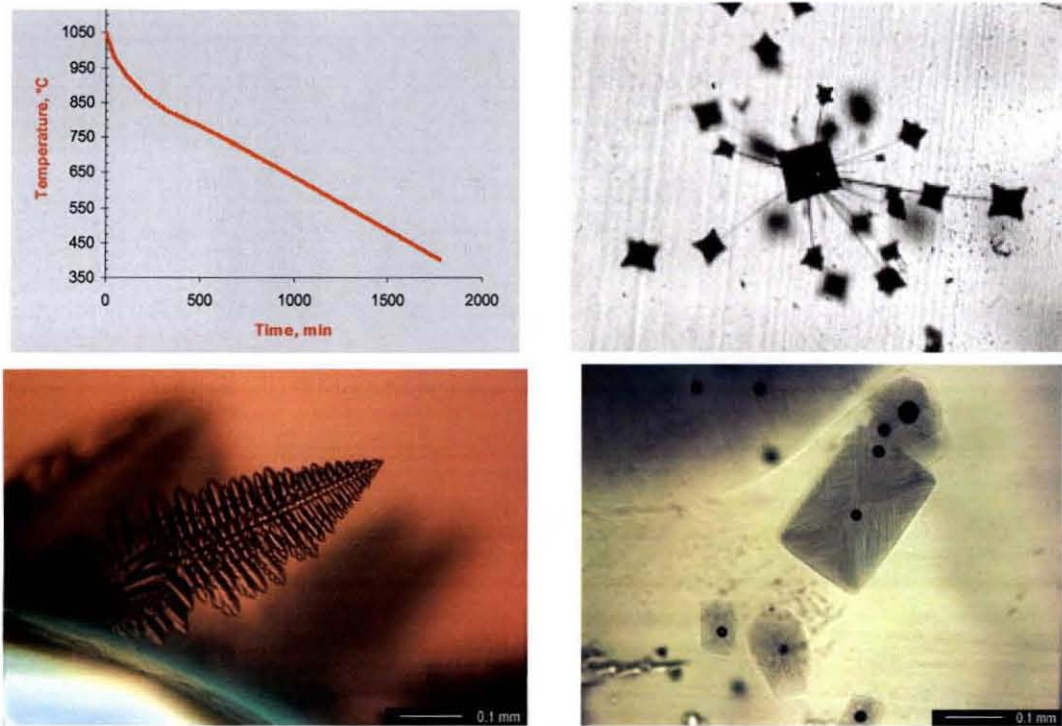


Fig. 6. (From top-left clockwise) Canister centerline cooling (for Hanford HLW glass), aggregate of spinel crystals and  $\text{RuO}_2$  needles, nepheline crystals, and baddeleyite dendrite.

## Conclusions

- 1) Waste glass can be efficiently formulated using the property-composition relationship. The results of calculations must be verified with experiments.
- 2) The formation of solids, segregation and migration of molten salts, and melt foaming can interfere with the waste-glass melting process. Crystallization can impact the quality of the final product. These phenomena need to be considered when formulating glass and determining the makeup of melter feeds.

- 3) Predicting the fate of glass over hundreds of thousands of years in a geologic repository based on various short-term corrosion tests remains a challenge. In a closed system, glass corrosion proceeds through four stages of which the last two (transition and final) are determined by mineral precipitation from the aqueous medium.
- 4) Bulk vitrification to accelerate LAW immobilization is still being evaluated. The major obstacle to its implementation on a large scale, the migration of waste species into the refractory lining, has been overcome by using fine-grain additives and adding cellulose to the melter feed.

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